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Phase Behavior of Weakly-segregated Multiblock Copolymers with Two-scale Periodic Architecture

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Abstract: The phase behavior of a melt of periodic two-scale multiblock copolymers has been theoretically studied in the framework of the Weak-Segregation Limit theory. The effect of the structural symmetry of the macromolecules on the vertex functions of the Landau free energy expansion is considered in detail. The existence of a thermodynamically stable mesophase with a two length-scale space periodicity has been revealed for a melt of monodisperse periodic heteropolymers.

Introduction

It is common knowledge that the molecular architecture of macromolecules exerts a major influence on various properties of block copolymers including elastomeric behavior, melt rheology, and toughness [1]. The most architecturally simple among binary linear block copolymers are those whose molecules consist of two or three blocks. Polymeric chains with a large number of blocks are traditionally referred to as multiblock copolymers [1,2], exemplified by segmented polyurethane [3,4] and segmented copolyesters [5]. The reaction between functionally terminated oligomers (oligomonomers) is a versatile method for producing such block copolymers. To have them composed of perfectly alternating segments, it is necessary to use oligomers with mutually reactive end groups, e.g., amino- and carboxyl groups. Such oligomers can react in the course of their heteropolycondensation only with each other and not with themselves. Another possibility for obtaining segmented copolymers is homopolycondensation of diblock oligomers terminated by two functional groups of

different types. This way of synthesis appears to be more convenient than heteropolycondensation where the stoichiometry condition for the initial monomer mixture should be strictly met to synthesize products of high molecular weight.

Involving in a step growth polymerization oligo- or macromonomers with a more complicated architecture, it is possible to prepare high-molecular weight multiblock copolymers whose chains have a chemical structure other than that of traditional segmented copolymers. Of particular interest in this respect are multiblock copolymers obtained by homopolycondensation of macromonomer in which at least one of two types of blocks is characterized by a bimodal distribution for its length. An example of such a macromonomer is shown in Fig.1. The structural factor $S(q)$ of these macromolecules can possess two maxima for some values of the parameters m and n [6]. This happens because a macromonomer with the chemical structure depicted in Fig.1 has two intrinsic length scales. Clearly, just the same scales will characterize the chemical structure of a periodic multiblock copolymer obtained by polycondensation of this macromonomer. The question arising here is to which extent the scattering and phase behavior of melts of the macromonomer and the products of its homopolycondensation will differ. In the simplest case, when the macromonomer is a diblock copolymer, such differences are of a quantitative rather than a qualitative character [7,8]. Whether this statement remains true for macromonomers whose chemical structure is characterized by two intrinsic length scales is an open question. So far no theoretical investigations on the thermodynamics of such periodic multiblock copolymers have been reported in literature. In the present paper such an examination is carried out in the framework of the Weak-Segregation Limit (WSL) theory for an incompressible melt of copolymers with chemical structures presented in Fig.1. One of the prime objectives we pursued analyzing theoretically the phase behavior of this system is to reveal the possibility of the existence of thermodynamically equilibrium mesophases, showing two different scales of the space periodicity. Simple physical considerations testify that this hypothesis is not without ground.

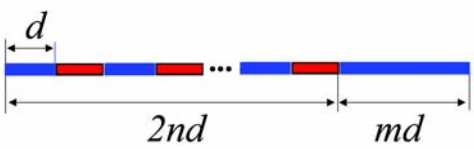

Fig. 1. A macromolecule with two intrinsic scales of space periodicity [6].

Indeed, the order-disorder transition (ODT) in this system is of second order. It occurs on the spinodal where the spatially-homogeneous state looses its thermodynamic stability with respect to the fluctuations with some wave vector $\mathbf{q}^*$ having modulus q^*. Essentially, the structural factor attains its maximum just at this value q^*. The ODT results in the formation near the spinodal of a mesophase wherein the density distribution of units of each type is described by a periodic function with period $\sim 1/q^*$. If the structural factor has two maxima at points q_{L}^* and q_{S}^*, the system looses its thermodynamic stability at the maximum where the value of $S(q)$ is larger. Here we are obviously dealing with a system whose spinodal curve has two branches corresponding to long and short scales of space periodicity, respectively. The most intriguing phase behavior of such a system should be expected in the vicinity of the line of double spinodal points (DSP) defined by equation $S\left(q_{\mathrm{L}}^*\right) = S\left(q_{\mathrm{S}}^*\right)$. On this line, two modes are excited simultaneously, the exponential growth of which saturates due to their interaction. Its specificity predetermines which particular mesophase will be formed as a result of the ODT. A two-scale mesophase is expected to be thermodynamically more preferable, provided modes of different scales interact noticeably stronger than one-scale modes. Otherwise the formation of some one-scale mesophase will be preferred.

To the authors knowledge, the theoretical consideration of two-scale mesophases has been carried out only in papers [9-15]. Using the WSL approach, De la Cruz et al [9,10] found the hexagonally perforated lamellar (HPL) mesophase to be stable for the incompressible melt of monodisperse diblock copolymers. Subsequent research [11] has thrown doubt on this conclusion. The possibility of the formation of stable two-scale mesophases has been predicted in melts of polydisperse segmented copolymers by Semenov et al [12,13]. However, from the results reported in these papers it ensues that one of the scales of space periodicity becomes infinitely large in the absence of polydispersity. Therefore such an approach does not permit describing two-scale mesophases in incompressible melts of monodisperse multiblock copolymers.

The first attempt to provide in the framework of the WSL approximation a description, free from uncontrollable assumptions, of two-scale mesophases in melts of multiblock copolymers was undertaken by Nap [14]. He managed to rigorously derive the expressions relating the coefficients of the amplitude expansion of the Landau free energy with the vertex functions of this functional for three particular two-scale mesophases. Later a general algorithm was put forward [15] to write down analogous expressions for any mesophases with a two-scale space periodicity.

In the present paper we employ this algorithm for calculating the coefficients of the amplitude expansion of the Landau free energy for periodic multiblock copolymer schematically depicted in Fig.2. With these coefficients calculated for different mesophases, we construct phase diagrams of its incompressible melt as a function of the structural parameter m for $n = 6$.

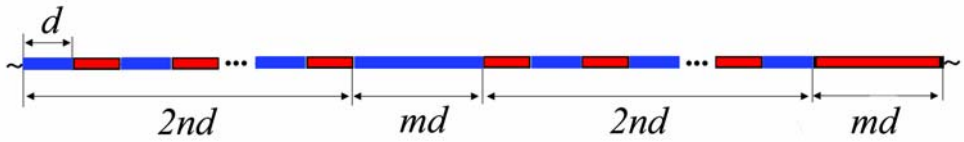

Fig. 2. Repeating fragment of an infinite block copolymer macromolecule.

The article is organized as follows. In the second Section, the microscopic WSL theory is briefly discussed for an incompressible melt of binary monodisperse block copolymers with long blocks. The third Section considers the types of symmetry of the chemical structure of these copolymers. The next two Sections study the effect of such symmetry of macromolecules on their correlation characteristics. In the sixth and seventh Sections the approach advanced is used to calculate the morphology diagrams and phase diagrams of two-scale periodical multiblock copolymers of a particular chemical structure.

Microscopic WSL theory

A consideration of the thermodynamic behavior of an incompressible melt of binary heteropolymers in the framework of the WSL theory [16-20] is based on the expansion of the Landau free energy functional $\mathcal{F}_{\mathrm{L}}[\psi]$ in powers of the order parameter (OP) $\psi(\mathbf{r}) = \psi_1(\mathbf{r}) = -\psi_2(\mathbf{r})$. The latter equals the deviation of the

local density $\rho_1(\mathbf{r})$ of units M_1 from its average value $\bar{\rho}_1$, divided by overall number M of monomeric units of both types, M_1 and M_2. As is customary in the WSL theory [16-20], we truncate the expansion of functional $\mathcal{F}_{\mathrm{L}}[\psi]$ at the fourth order term. In the Fourier representation, this expansion looks as follows

$$\mathcal{F}\left[\tilde{\psi}(\mathbf{q})\right] = \frac{1}{TM}\mathcal{F}_{\mathrm{L}}\left[\tilde{\psi}(\mathbf{q})\right] = \frac{1}{2!}\sum_{\{\mathbf{q}\}}\tilde{\Gamma}^{(2)}(\mathbf{q},-\mathbf{q})\tilde{\psi}(\mathbf{q})\tilde{\psi}(-\mathbf{q}) +$$

$$\frac{1}{3!}\sum_{\{\mathbf{q}_i\}}\tilde{\Gamma}^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\tilde{\psi}(\mathbf{q}_1)\tilde{\psi}(\mathbf{q}_2)\tilde{\psi}(\mathbf{q}_3)\delta_{\mathrm{K}}(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3) + \tag{1}$$

$$\frac{1}{4!}\sum_{\{\mathbf{q}_i\}}\tilde{\Gamma}^{(4)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)\tilde{\psi}(\mathbf{q}_1)\tilde{\psi}(\mathbf{q}_2)\tilde{\psi}(\mathbf{q}_3)\tilde{\psi}(\mathbf{q}_4)\delta_{\mathrm{K}}(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4)$$

Here T stands for the temperature in energetic units, $\delta_{\mathrm{K}}(\mathbf{q})$ is the Kronecker delta, and $\tilde{\psi}(\mathbf{q})$ represents the Fourier transform of OP, while $\tilde{\Gamma}^{(2)}(\mathbf{q}_1,\mathbf{q}_2)$, $\tilde{\Gamma}^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)$ and $\tilde{\Gamma}^{(4)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$ denote the second, third and fourth order vertex function, respectively.

Functions $\tilde{\Gamma}^{(3)}$ and $\tilde{\Gamma}^{(4)}$ are controlled exclusively by the chemical structure of macromolecules of the block copolymer under examination, whereas $\tilde{\Gamma}^{(2)}$ depends in addition on the temperature [16-20]. The chemical structure of a macromolecule is known to be completely characterized by the set of chemical correlators [21,22]. The simplest among them, the two-point correlator $Y^{(2)}_{\alpha_1\alpha_2}(\Delta\xi)$, represents the probability for a pair of monomeric units located at distance $\Delta\xi$ along a macromolecule to be of types α_1 and α_2. The three-point correlator $Y^{(3)}_{\alpha_1\alpha_2\alpha_3}(\Delta\xi_1,\Delta\xi_2)$ is equal to the probability for a triple of units located at distances $\Delta\xi_1$ and $\Delta\xi_2$ to be of types α_1, α_2 and α_3. The l-point correlator with arbitrary l is defined in a similar manner. A general algorithm has been formulated [23] that permits expressing the vertex function $\tilde{\Gamma}^{(l)}$ through generating functions of s-point chemical correlators (gfCC-s) $W^{(s)}_{\alpha_1\ldots\alpha_s}(y_1,\ldots,y_{s-1})$ with $s \le l$. Making use of this algorithm, we will take into account

the specific features of the block copolymers under consideration. Of our concern in the present paper are monodisperse block copolymers, all blocks of which are sufficiently long. In this case, the variable ξ characterizing the position of a monomeric unit in a macromolecule may be taken to be a continuous rather than a discrete variable. So, the expression for gfCC-l can be written down as

$$W^{(l)}_{\alpha_1\ldots\alpha_l}\left(y_1,\ldots,y_{l-1}\right)=\frac{d^{l-1}}{2\mathcal{N}}\int\limits_{-\mathcal{N}}^{\mathcal{N}}\left\{\int\limits_{-\mathcal{N}}^{\xi_1}\cdots\left\{\int\limits_{-\mathcal{N}}^{\xi_{l-1}}U^{(l)}_{\alpha_1\ldots\alpha_l}\left(\xi_1,\ldots,\xi_l;y_1,\ldots,y_{l-1}\right)d\xi_l\right\}\cdots d\xi_2\right\}d\xi_1$$

$$U^{(l)}_{\alpha_1\ldots\alpha_l}\left(\xi_1,\ldots,\xi_l;y_1,\ldots,y_{l-1}\right)\equiv p_{\alpha_l}\left(\xi_l\right)\prod_{i=1}^{l-1}\left\{p_{\alpha_i}\left(\xi_i\right)\exp\left[-y_i\left(\xi_i-\xi_{i+1}\right)\right]\right\} \tag{2}$$

where the variables $y_i\left(i=1,l-1\right)$ are proportional to the square of the gyration radius R_{G} of a Gaussian macromolecule consisting of d units with length a

$$y_i=R_{\mathrm{G}}^2Q_i^2,\quad R_{\mathrm{G}}^2=\frac{a^2d}{6},\quad Q_i\equiv\left|\mathbf{Q}_i\right|,\quad \mathbf{Q}_i=\sum_{j=1}^{i}\mathbf{q}_j \tag{3}$$

The variables $\xi_1,\xi_2,\ldots,\xi_l$ of in expression (2) represent the distances from the midpoint of a macromolecule of length $2N=2\mathcal{N}d$ divided by length $d\gg1$ of the shortest block. The profile $p_\alpha\left(\xi\right)\left(\alpha=1,2\right)$ represents the probability to find an α-th type unit at point ξ of a macromolecule.

Given the expressions for gfCC-l, one can obtain the vertex functions of expansion (1) by means of the following formulas [16-20]

$$\tilde{\Gamma}^{(2)}\left(\mathbf{q},-\mathbf{q}\right)=H\left(q\right)-2\chi,\quad H\left(q\right)\equiv\frac{\tilde{\theta}_{11}\left(q\right)+2\tilde{\theta}_{12}\left(q\right)+\tilde{\theta}_{22}\left(q\right)}{\tilde{\theta}_{11}\left(q\right)\tilde{\theta}_{22}\left(q\right)-\tilde{\theta}_{12}^2\left(q\right)},\quad q=\left|\mathbf{q}\right| \tag{4}$$

$$\tilde{\Gamma}^{(3)}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)=-\sum_{\{\alpha,\beta,\gamma\}}\tilde{\theta}^{(3)}_{\alpha\beta\gamma}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)z_\alpha\left(q_1\right)z_\beta\left(q_2\right)z_\gamma\left(q_3\right),$$

$$z_\alpha\left(q\right)\equiv\tilde{\theta}^{-1}_{\alpha1}\left(q\right)-\tilde{\theta}^{-1}_{\alpha2}\left(q\right) \tag{5}$$

$$\tilde{\Gamma}^{(4)}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\sum_{\{\alpha,\beta,\gamma,\delta\}}\left\{-\tilde{\theta}^{(4)}_{\alpha\beta\gamma\delta}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)+\right.$$

$$\sum_{\{\mu,\nu\}}\left[\tilde{\theta}^{(3)}_{\alpha\beta\mu}\left(\mathbf{q}_1,\mathbf{q}_2,-\mathbf{q}_1-\mathbf{q}_2\right)\tilde{\theta}^{-1}_{\mu\nu}\left(\mathbf{q}_1+\mathbf{q}_2\right)\tilde{\theta}^{(3)}_{\alpha\beta\nu}\left(\mathbf{q}_3,\mathbf{q}_4,\mathbf{q}_1+\mathbf{q}_2\right)+\right.$$

$$\tilde{\theta}^{(3)}_{\alpha\beta\mu}\left(\mathbf{q}_1,\mathbf{q}_3,-\mathbf{q}_1-\mathbf{q}_3\right)\tilde{\theta}^{-1}_{\mu\nu}\left(\mathbf{q}_1+\mathbf{q}_3\right)\tilde{\theta}^{(3)}_{\alpha\beta\nu}\left(\mathbf{q}_2,\mathbf{q}_4,\mathbf{q}_1+\mathbf{q}_3\right)+ \tag{6}$$

$$\left.\left.\tilde{\theta}^{(3)}_{\alpha\beta\mu}\left(\mathbf{q}_1,\mathbf{q}_4,-\mathbf{q}_1-\mathbf{q}_4\right)\tilde{\theta}^{-1}_{\mu\nu}\left(\mathbf{q}_1+\mathbf{q}_4\right)\tilde{\theta}^{(3)}_{\alpha\beta\nu}\left(\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_1+\mathbf{q}_4\right)\right]\right\}\times$$

$$z_\alpha\left(q_1\right)z_\beta\left(q_2\right)z_\gamma\left(q_3\right)z_\delta\left(q_4\right)$$

Here χ is the Flory-Huggins parameter, while $\tilde{\theta}^{-1}_{\alpha\beta}\left(q\right)$ stand for the elements of the matrix which is the inverse of the structural matrix with elements $\tilde{\theta}_{\alpha\beta}\left(q\right)$. Every element $\tilde{\theta}^{(l)}_{\alpha_1\ldots\alpha_l}$ of tensor $\tilde{\theta}^{(l)}$ represents the sum of $l!$ items. The first of them is the gfCC-l (2), whereas the rest are obtained from it by permutation of labels of all l points of the l-point correlator [24]. Since we are dealing with a melt of monodisperse heteropolymers, expressions (4)-(6) do not comprise non-local terms [25]. Essentially, the formulas for the vertex functions derived earlier [23] instead of tensors $\tilde{\theta}^{(l)}$ contain tensors $X^{(l)}$ representing the Fourier transforms of the physical correlators of monomeric units' densities in an individual molecule. Each of these tensors is a sum of several items differing by order with respect to large parameter $d\gg 1$, which is specified by the number of coinciding points in the l-point correlator. At $d\to\infty$ it is evidently possible to restrict oneself in expressions for $X^{(l)}_{\alpha_1\ldots\alpha_l}$ to the main term $\tilde{\theta}^{(l)}_{\alpha_1\ldots\alpha_l}$ whose order with respect to this parameter is $\left(l-1\right)$.

Therefore, to get vertex functions $\tilde{\Gamma}^{(l)}$ (4)-(6) of block copolymers with given chemical structure, it is necessary to find expressions for $s!$ functions gfCC-s for all $s\le l$. This procedure seems to be quite a time consuming computational task. For symmetric copolymers, such a calculation, however, is markedly simplified because the number of independent components of tensor $W^{(l)}$ is smaller in this case.

Symmetry of macromolecules

When describing various kinds of symmetry of the chemical structure of binary block copolymer macromolecules, it is convenient to resort to the terminology accepted in the theory of black and white (magnetic) groups [26,27], assuming units M_1 and M_2 are taken as being colored black and white. Following this theory, asymmetric (Fig.3a), symmetric (Fig.3c) and anti-symmetric (Fig.3b) block copolymer macromolecules should be distinguished. Mathematically this means that the two latter profiles $p_1(\xi)$ and $p_2(\xi)$ satisfy the following relationships

$$\text{I. } p_1(\xi) = p_1(-\xi),\ p_2(\xi) = p_2(-\xi), \quad \text{II. } p_1(\xi) = p_2(-\xi),\ p_2(\xi) = p_1(-\xi) \tag{7}$$

According to formulas (7-I), for symmetric macromolecules the profiles of monomeric units are invariant with respect to inversion which means the reversal of direction of the conventional movement along a macromolecule. In the case of anti-symmetric macromolecules, this invariance takes place under anti-inversion when simultaneous reversal of direction of such a movement is followed by “recoloring” of the monomeric units $\mathrm{M}_1 \leftrightarrow \mathrm{M}_2$. All symmetry operations of any macromolecule form its black and white point group [26,27]. As a result of such a recoloring, an α-th type unit becomes an α'-th type one. It is evident that the midpoint of a macromolecule is obviously its centre of inversion and anti-inversion for a symmetric and anti-symmetric macromolecule, respectively. Note, a necessary (though insufficient) condition for the structural anti-symmetry of macromolecules is that the fractions X_1 and X_1 of units M_1 and M_2 in them equal 1/2. It is easy to show that for anti-symmetric binary incompressible copolymers, all vertex functions of odd degree, and, particularly, $\tilde{\Gamma}^{(3)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$, in the Landau free energy expansion (1) are identically equal to zero.

Apart from point-group operation’s symmetries, for macromolecules of infinite length, the translation-invariance symmetry is possible [28]. Such a symmetry is inherent to macromolecules whose profiles, $p_\alpha(\xi)$ $(\alpha = 1, 2)$, are periodic functions with period $2L$

$$p_\alpha(\xi) = p_\alpha(\xi + 2Lk) \tag{8}$$

where k is an arbitrary integer. Macromolecules, close to periodic ones, can be obtained by polycondensation of a large number $\mathcal{N}/L \gg 1$ of identical macromonomers with length $2Ld$. A fundamental translational repeat unit of such periodic macromolecules can be referred to as an elementary cell. Generally speaking, any fragment of a macromolecule of length $2Ld$ can be chosen as such a cell. Obviously, all properties of a periodic macromolecule can be described by considering a single cell. It is clear that the fraction of α-type units in a cell coincides with component X_α of the vector of the chemical composition of a macromolecule.

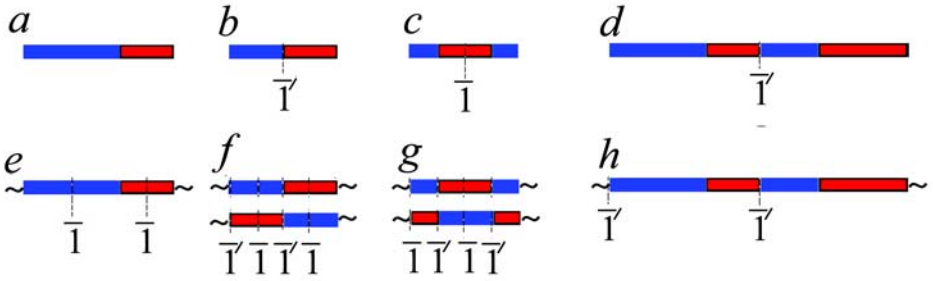

Fig. 3. Properties of structure symmetry of finite (a, b, c, d) and infinite periodic (e, f, g, h) macromolecules of binary block copolymers. The cells are depicted for the second of them, obtained by polycondensation of the first ones. Symbols $\bar{1}$ and $\bar{1}'$ denote the centers of inversion and anti-inversion, respectively. Among all elements of the symmetry of a macromolecule, the element of the symmetry of an individual cell is presented in boldface.

Fig.3 presents some block copolymers exemplifying their structure symmetry. Infinite macromolecules (e-h) qualitatively differ from finite ones (a-d) is the possibility of the presence in the point group of the first of them of both inversion and anti-inversion operations with non-coinciding centers (f, g). Each element of the black and white space group [26,27] of a periodic macromolecule represents the product of some element of its point group and the operation of translation along the macromolecule over an arbitrary interval whose length is divisible by $2Ld$. That is the reason why the overall number of such centers throughout a macromolecule is infinite, while in an elementary cell it is finite. Since for any periodic macromolecule of block copolymers

an infinite number of possibilities exists of choosing an elementary cell, the point group of this macromolecule is the sum of point groups of the elementary cells chosen in all possible ways. For example, different cells of the same periodic macromolecule possessing anti-inversion and inversion centers, respectively, are depicted in Fig.3f and 3g. Any other choice will result in a non-symmetrical cell. Thus, to reveal all elements of the structural symmetry of a periodic macromolecule with arbitrary chemical structure, one should specify all different symmetric and anti-symmetric cells of this macromolecule. It is possible to obtain their complete set by shifts in both directions with respect to the midpoint of some fixed cell to the distances which are less than half of its length. In doing so, the points of this cell at which the midpoints of other cells fall will be the centers of inversion and anti-inversion of the periodic macromolecule in hand. The above-formulated algorithm will be used below to find elements of the symmetry of a block copolymer of two-scaled architecture portrayed in Fig.2.

In what follows we will discuss the simplifications that arise when calculating the correlation characteristics of the chemical structure of block copolymers showing some structural symmetry. Such characteristics are tensors $W^{(l)}$ and $\tilde{\theta}^{(l)}\left(l=2,3,4\right)$, each of which will be studied individually for finite and infinite periodic macromolecules.

Structural matrix

Polymer chains of finite length

Let us point out first some general properties of tensor $W^{(2)}$ independent of the chemical structure of finite macromolecules. There are obvious stoichiometric relationships

$$W_{12}^{(2)}\left(y\right)+W_{11}^{(2)}\left(y\right)=J_{1}^{(2)}\left(y\right),\quad W_{21}^{(2)}\left(y\right)+W_{22}^{(2)}\left(y\right)\equiv J_{2}^{(2)}\left(y\right) \tag{9}$$

where the following designation is used

$$J_\alpha^{(2)}(y) \equiv \frac{d}{2\mathcal{N}} \int_{-\mathcal{N}}^{\mathcal{N}} \int_{-\mathcal{N}}^{\xi_1} p_\alpha(\xi_1) e^{-y(\xi_1-\xi_2)} d\xi_2 d\xi_1 =$$

$$\frac{d}{2\mathcal{N}y} \int_{-\mathcal{N}}^{\mathcal{N}} p_\alpha(\xi) \left[1 - e^{-y(\mathcal{N}+\xi)}\right] d\xi \quad (\alpha = 1,2) \tag{10}$$

By virtue of these relationships, for the calculation of components of tensor $W^{(2)}$, it will suffice instead of four double integrals to calculate only two double and one single integral, because the sum of two single integrals (10) is proportional to the Debye function g_{D}

$$I^{(2)}(y) \equiv J_1^{(2)}(y) + J_2^{(2)}(y) = \mathcal{N} d\, g_{\mathrm{D}}(2\mathcal{N}y),$$

$$g_{\mathrm{D}}(x) \equiv \frac{2}{x^2}\left(x - 1 + e^{-x}\right) \tag{11}$$

In the case of symmetrical (7-I) and anti-symmetrical (7-II) block copolymers, for any values of variable y the following relationships hold

$$\mathrm{I}.\, W_{12}^{(2)}(y) = W_{21}^{(2)}(y), \quad \mathrm{II}.\, W_{11}^{(2)}(y) = W_{22}^{(2)}(y) \tag{12}$$

Periodic polymer chains

For arbitrary periodic macromolecules with a cell size $2Ld$, functions $W_{\alpha\beta}^{(2)}(y)$ can be written down as

$$W_{\alpha\beta}^{(2)}(y) = R_{\alpha\beta}(y) + \frac{N_{\alpha\beta}(y)}{1 - e^{-2Ly}} = \frac{e^{Ly} R_{\alpha\beta}(y) + e^{-Ly} R_{\alpha\beta}(-y)}{2\mathrm{sh}\, Ly}, \tag{13}$$

where the following notation is adopted

$$R_{\alpha\beta}(y) \equiv \frac{d}{2L} \int_{-L}^{L} \int_{-L}^{\xi_1} U_{\alpha\beta}^{(2)}(\xi_1, \xi_2; y)\, d\xi_2 d\xi_1,$$

$$N_{\alpha\beta}(q) \equiv e^{-2Ly} \left[R_{\alpha\beta}(y) + R_{\alpha\beta}(-y)\right] \tag{14}$$

From the first equality of formula (13) it ensues that tensor $W^{(2)}$ is the sum of two tensors. The first allows for the chemical correlations in the positions of monomeric

units inside a cell, whereas the second one takes into account the correlations of units of the cell of interest with units of the remaining cells. The division into such a sum was noted for the first time in [7] for multiblock copolymer with a cell, which architecture coincides with that of a diblock copolymer. At point $y = 0$ the components of the first of these two tensors are analytic, while the components of the second one have first order pole with residue $dX_\alpha X_\beta$. It is clear that the components of tensor $W^{(2)}(y)$ are odd functions, and, consequently, the expansion of these functions into the Laurent series near point $y = 0$ contains only odd degrees of argument y.

Of considerable interest is to discuss the asymptotic behavior of the spinodal function $H(q)$ (4) at $q \to 0$ and $q \to \infty$. The numerator of this function is equal to $2I^{(2)}(y) = 2d/y$. To analyze the behavior of the denominator at $y \to 0$ and $y \to \infty$, it is convenient to make use of expression

$$W^{(2)}_{\alpha\beta}(y) = \frac{d}{y} X_\alpha X_\beta + w_{\alpha\beta}(y), \text{ where } w_{\alpha\beta}(y) \equiv (-1)^{\alpha+\beta} w(y), \quad w(0) = 0 \quad (15)$$

connecting generating functions $W^{(2)}_{\alpha\beta}(y)$ and $w^{(2)}_{\alpha\beta}(y)$ of reducible and irreducible chemical correlators, respectively. Recourse to the definition of the elements of the structural matrix $\tilde{\theta}_{\alpha\beta}(q) = W^{(2)}_{\alpha\beta}(y) + W^{(2)}_{\beta\alpha}(y)$ and subsequent substitution of relationship (15) for $W^{(2)}_{\alpha\beta}(y)$ into formula (4) yields a simple expression for the spinodal function and its asymptotics at $q \to 0$

$$H(q) = \frac{1}{2w(y)} \Rightarrow \frac{1}{2w'(0)\,y} + O(y), \quad y = R_G^2 q^2 \quad (16)$$

Using the asymptotic $y \to \infty$ expression

$$w(y) = \frac{d}{y} X_1 X_2 + O\left(\frac{1}{y^2}\right) \quad (17)$$

we arrive at the known [30] asymptotics of the function $H(q)$ at $q \to \infty$

$$H(q) = \frac{y}{2dX_1X_2} + O(1) \qquad (18)$$

As it follows from expressions (16) and (18), the character of the asymptotic dependence of vertex function $\tilde{\Gamma}^{(2)}$ (4) on the modulus q of wave vector $\mathbf{q}$ will for infinite periodic macromolecules be identical to that for finite macromolecules, namely, $H(q) \sim q^{-2}$ at $q \to 0$ and $H(q) \sim q^{2}$ at $q \to \infty$. Essentially, the proportionality coefficient in the second asymptotics is controlled exclusively by the copolymer composition, whereas the coefficient in the first one is governed also by the chemical structure of its macromolecules.

Effect of the symmetry of the chemical structure on its correlation characteristics

As already mentioned above, in the case of block copolymers of arbitrary chemical structure, each component of the tensor-function $\tilde{\theta}^{(l)}_{\alpha_1\ldots\alpha_l}(\mathbf{q}_1,\ldots,\mathbf{q}_l)$ represents the sum of $l!$ items, each being obtained from gfCC-*l* (2) by a permutation of labels. So, this tensor-function possesses, by definition, the symmetry with respect to simultaneous permutation of indices and wave vectors of any number of its l points. The conditions of structural symmetry and/or anti-symmetry of macromolecules establish certain equalities between different components of tensor $W^{(l)}$, taken at distinct points of $(l-1)$-dimensional space $\{y_i\}$. This is the reason why under examination of symmetrical macromolecules, the number of items in the sum defining the component of $\tilde{\theta}^{(l)}$ will be twice less than $l!$. Employment of the relationships of the symmetry and anti-symmetry permits writing down the equalities between certain components of the tensor-function $\tilde{\theta}^{(l)}$, i.e., to reveal the dependence of its symmetry on the structural symmetry of the macromolecules.

It can be readily shown that from expression (2) and definition (7) of symmetric and anti-symmetric block copolymers the following relationships ensue

$$\text{I.}\quad W^{(l)}_{\alpha_1\ldots\alpha_l}\left(y_1,\ldots,y_{l-1}\right)=W^{(l)}_{\alpha_l\ldots\alpha_1}\left(y_{l-1},\ldots,y_1\right),$$
$$\text{II.}\quad W^{(l)}_{\alpha_1\ldots\alpha_l}\left(y_1,\ldots,y_{l-1}\right)=W^{(l)}_{\alpha_l'\ldots\alpha_1'}\left(y_{l-1},\ldots,y_1\right) \tag{19}$$

where subscript α_i' denotes the type of a monomeric unit resulting from an α_i-th type unit upon its re-coloring. From formulas (19-II) and the definition of the tensor-function $\tilde{\theta}^{(l)}$, the following relationships between its components for anti-symmetric block copolymers ensue

$$\tilde{\theta}^{(l)}_{\alpha_1\ldots\alpha_l}\left(\mathbf{q}_1,\ldots,\mathbf{q}_l\right)=\tilde{\theta}^{(l)}_{\alpha_1'\ldots\alpha_l'}\left(\mathbf{q}_1,\ldots,\mathbf{q}_l\right) \tag{20}$$

The results of the employment of general expressions (19), (20) in the particular cases $l=3$ and $l=4$ are presented in appendices A and B, respectively.

Periodic macromolecule with two-scale cell

The application of the above-formulated approach will be exemplified below by the construction of the phase diagram of a block copolymer whose chemical structure is depicted in Fig.2. Its macromolecules are at the same time symmetric and anti-symmetric. As it is evident from Fig.4, its cell can be chosen non-symmetric (a), symmetric (b) and anti-symmetric (c).

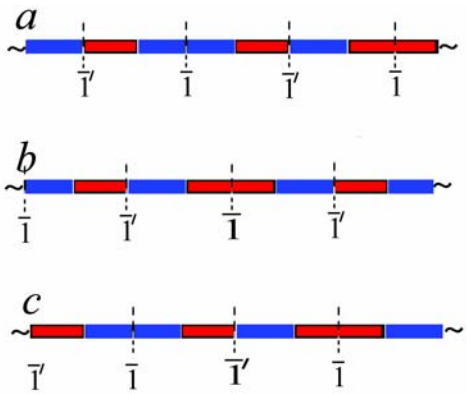

Fig. 4. Different cells that can be chosen in the periodic block copolymer depicted in Fig.2 at $n=1,\quad m\neq 1$. Among all elements of the symmetry of a macromolecule, the element of the symmetry of an individual cell is presented in boldface.

In the case under examination $\tilde{\theta}_{\alpha\beta}\left(q\right)=2W_{\alpha\beta}^{(2)}\left(y\right)$, and among the components of tensor $W^{(2)}\left(y\right)$ only one is independent. $W_{11}^{(2)}\left(y\right)$ can be chosen as such a component, the expression for which is presented in Appendix C. At $q\to 0$, the spinodal function $H\left(q\right)$ (4) is described by asymptotic formula (16) where

$$w'\left(0\right)=\frac{m^3+8n+6\left(m-2\right)mn}{48\left(m+2n\right)} \tag{21}$$

Particularly, when $m=1$ this formula reduces to that derived earlier [30].

We have calculated classification diagrams of the spinodal function $H\left(q\right)$ of the periodic multiblock copolymer presented in Fig.2 and of the melt of macromonomers whose chemical structure is just that of an individual cell. The comparison of these diagrams depicted in Fig.5 shows that being qualitatively identical, quantitatively they slightly differ. However, the phase behavior of the two systems in hand is expected to differ qualitatively. The reason is that the macromonomers under consideration exhibit the anti-symmetry property only at $m=1$, whereas infinite macromolecules obtained by their polycondensation are anti-symmetric for any m. For the latter, the vertex function $\tilde{\Gamma}^{(3)}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)$ (5) is identically equal to zero for any values of the structure parameters m and n. In contrast, for the former $\tilde{\Gamma}^{(3)}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)=0$ for every fixed n on a finite set of values $\left\{m_{\mathrm{pc}}\left(n\right)\right\}$ [31]. In the case of non-symmetric block copolymers of finite length, the order-disorder transition (ODT) will be of second order provided $m=m_{\mathrm{pc}}\left(n\right)$, and of first order when this condition is not met. This is one of their most striking distinctions from anti-symmetric periodic block copolymers, for which such a transition proceeds by second order for any values of the structure parameters. Therefore, the type of ODT is dissimilar between the melt of macromonomers in hand and the melt of periodic macromolecules obtained by their polycondensation. Essentially, in the melt of macromonomers for which the value of parameter m is close to m_{pc}, the ODT will be a weakly first order phase transition. To construct a phase diagram in this case, the WSL theory may be invoked. Far from

points $\left(m_{\mathrm{pc}}, n\right)$, this theory does not work, because the range of alteration of OP $\psi\left(\mathbf{r}\right)$ in a mesophase formed is wide enough, and macromonomers' conformations markedly differ from the Gaussian ones [17].

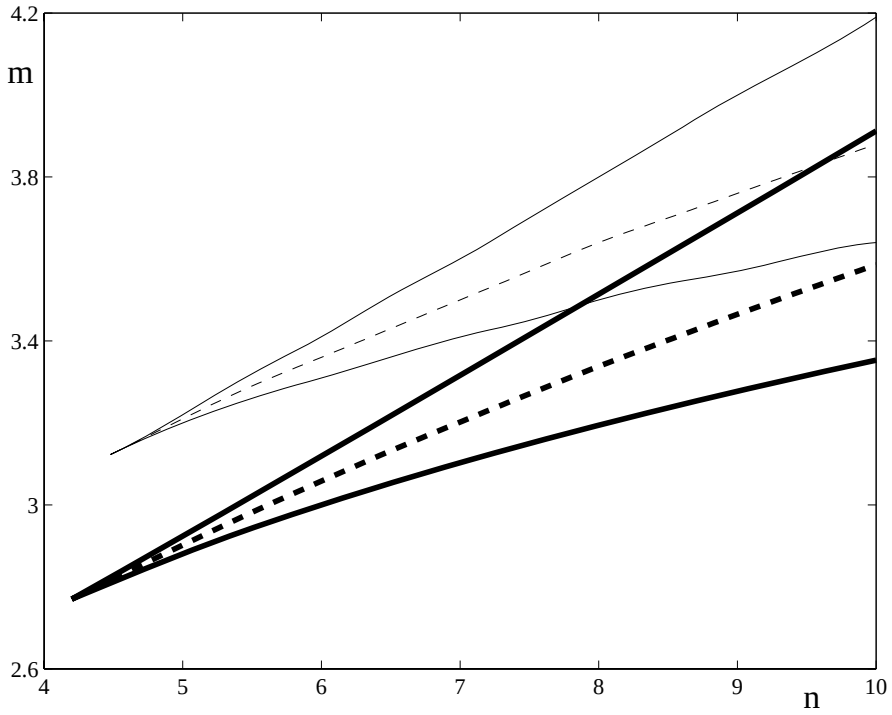

Fig. 5. Classification diagrams of the function $H\left(q\right)$ (4) for the multiblock copolymer shown in Fig.2 (heavy lines) and for a melt of macromonomers having the chemical structure of its individual cell presented in this figure (thin lines). Outside every cusp, the function $H\left(q\right)$ has at $q = q^*$ only one minimum, whereas inside every cusp, it has two minima, at $q = q_{\mathrm{L}}^*$ and $q = q_{\mathrm{S}}^*$ ($q_{\mathrm{L}}^* < q_{\mathrm{S}}^*$). Inequalities $H\left(q_{\mathrm{L}}^*\right) > H\left(q_{\mathrm{S}}^*\right)$ and $H\left(q_{\mathrm{L}}^*\right) < H\left(q_{\mathrm{S}}^*\right)$ hold, respectively, in the lower and upper halves of cusps, whereas on the dashed lines, the equality $H\left(q_{\mathrm{L}}^*\right) = H\left(q_{\mathrm{S}}^*\right)$ holds.

Morphology diagram

As is customary in the WSL theory [16-20], we will search for the minimum of the functional (1) on a set of candidate mesophases. Their spatial symmetry predetermines the appearance of the trial functions of the OP that are the sum of k

pairs of harmonics with wave vectors $\left\{\mathbf{q}^{(i)},-\mathbf{q}^{(i)}\right\}_k$ and phases $\left\{\varphi_i,-\varphi_i\right\}_k$ [16-20]. In the framework of the first-harmonic approximation [16-20], the modulus $q^{(i)}$ of wave vector $\mathbf{q}^{(i)}$ equals the modulus of one of the wave vectors corresponding to distinct branches of the spinodal, which can be found from the solution of the following equations

$$H\left(q^*\right)-2\chi_{\mathrm{sp}}=0,\quad H'\left(q^*\right)=0,\quad H''\left(q^*\right)>0 \tag{22}$$

Here the spinodal function $H\left(q\right)$ is defined by formula (4), while χ_{sp} denotes the value of parameter χ on the spinodal. A melt of periodic macromolecules whose chemical structure is shown in Fig.1 with values of parameters m and n that fall outside or inside the cusp in Fig.4 will be described by one or two spinodal branches, respectively. In the latter case, wave vectors with moduli q_{L}^* and q_{S}^* correspond to these branches. Thus, OP $\tilde{\psi}\left(\mathbf{q}\right)$ in the general case will have two components [15]

$$\begin{aligned}\tilde{\psi}\left(\mathbf{q}\right)=\frac{A}{\sqrt{k}}\sum_{j_1=1}^{k_1}\left[e^{i\varphi_{j_1}}\delta_{\mathrm{K}}\left(\mathbf{q}-\mathbf{q}_{\mathrm{L}}^{(j_1)}\right)+e^{-i\varphi_{j_1}}\delta_{\mathrm{K}}\left(\mathbf{q}+\mathbf{q}_{\mathrm{L}}^{(j_1)}\right)\right]+\\ \frac{B}{\sqrt{k}}\sum_{j_2=1}^{k_2}\left[e^{i\varphi_{j_2}}\delta_{\mathrm{K}}\left(\mathbf{q}-\mathbf{q}_{\mathrm{S}}^{(j_2)}\right)+e^{-i\varphi_{j_2}}\delta_{\mathrm{K}}\left(\mathbf{q}+\mathbf{q}_{\mathrm{S}}^{(j_2)}\right)\right]\end{aligned} \tag{23}$$

where the designations $\left|\mathbf{q}_{\mathrm{L}}^{(j_1)}\right|=q_{\mathrm{L}}^*,\quad \left|\mathbf{q}_{\mathrm{S}}^{(j_2)}\right|=q_{\mathrm{S}}^*,\quad k_1+k_2=k$ are employed. If any of the amplitudes, A or B, vanishes, the mesophase (if available) associated with this OP will have only one space periodicity scale that is inversely proportional to q_{L}^* ($A\neq 0$) or q_{S}^* ($B\neq 0$). A mesophase with OP having two nonzero amplitudes will be referred to as a two-scale mesophase [32]. Substitution of functions (23) into expression (1) reduces this functional to the function representing the amplitude expansion of the Landau free energy whose coefficients are controlled by both spatial symmetry of the candidate mesophase and the chemical structure of the macromolecules in point [15]. Successive minimization of this function with respect to amplitudes A, B and the phases $\left\{\varphi_i\right\}_k$ carried out for all candidate mesophases

yields a set of local minima, each corresponding to a particular mesophase. That of them whose free energy is minimal is thermodynamically stable, whereas the rest are metastable.

The sequence of stable mesophases and values of parameter χ at the points of the phase transitions between them with changing temperature constitutes the phase diagram. In the statistical thermodynamics of incompressible melts of block copolymers a phase diagram is taken to mean the *morphology diagram* [33]. The latter is constructed in a two- or three-dimensional space of parameters, the set of which apart from χ, also includes some parameters of the macromolecular chemical structure. Since they are not thermodynamic variables, the morphology diagram is not, strictly speaking, a phase diagram.

In order to construct a morphology diagram of the melt of a block copolymer with macromolecules whose chemical structure is shown in Fig.2, we selected the following set of candidate mesophases. Within the region of parameters m and n falling outside the cusp (Fig.5), all candidate mesophases are one-scale ones. Among them we examined [with Hermann-Mauguin symbols from Refs.(34,35)] lamellar (LAM, $\bar{1}$), hexagonal (HEX, $p6mm$), Body-centered cubic (BCC, $Im\bar{3}m$), BCC2 [36] ($I\bar{4}3d$), face centered cubic (FCC, $Fm\bar{3}m$) and simple cubic (SC, $Pm\bar{3}m$) mesophases. Since the double gyroid ($Ia\bar{3}d$) mesophase [37] cannot be described in the framework of the first harmonic approximation, it is left out of consideration in this paper. The square mesophase has also been left out of consideration, because such a mesophase was shown [38] incapable of being stable even locally. In the region of structure parameters falling inside the cusp (Fig.5), it is necessary to consider the double set of the above-listed one- scale mesophases. This is indispensable since each of them can be constructed for wave vectors whose modulus is q_{L}^{*} (mesophase-L) and q_{S}^{*} (mesophase-S). Besides, in this region we have also examined such two-scale mesophases as stretched hexagonal (StHEX, $c2mm$), constrained hexagonal (CnHEX, $c2mm$), rectangular (REC, $p2mm$) and two tetragonal (TET1 and TET2, $P4/mmm$) mesophases [15]. Crystal lattice of each of two latter is obtained from the crystal lattice of the SC mesophase by deformation along one of three mutually perpendicular directions. So, the lattice of

the TET1 (TET2) mesophase is the result of the compressing (stretching) of the lattice of the SC-L (SC-S) mesophase. Expressions for the coefficients of the amplitude expansion of the Landau free energy for all mesophases mentioned above are reported in paper [15]. As for their numerical values, these can be calculated using formulas for the vertex function $\tilde{\Gamma}^{(4)}$ (6) and the properties of the structure symmetry and anti-symmetry presented in Appendices A and B.

As stated in the foregoing, due to the anti-symmetry of the periodic macromolecules of the block copolymer of interest, the ODT in its melt occurs on the spinodal and is of second order. However, its morphology diagram (Fig.6) qualitatively differs from that for the traditional anti-symmetric macromolecules (i.e., functionally terminated diblock copolymers [16] and multi-block copolymer obtained by their polycondensation [7]). The fact is that in the melt of the two-scale block copolymer at hand, the stable mesophase formed as a result of the ODT can differ from LAM. A specific feature of the morphology diagram (Fig.6) is the presence at $3.36 \le m < 3.40$ of secondary first order phase transitions, SC-L $\rightarrow$ TET1 and TET1 $\rightarrow$ BCC-S, proceeding with increasing parameter χ [32]. When its values fall in the region between points of these transitions, the two-scale TET1 mesophase turns out to be stable having the lowest free energy among all the above-considered one-scale mesophases.

The lines of the first-order phase transitions in Fig.6 are cut off at $m \cong 3.40$ because the Landau theory becomes incorrect as m gets close to the value $m_{+} = 3.407$ corresponding to the upper border of the cusp (Fig.5). In this region, the spinodal function $H\left(q\right)$ is so flat near its minimum at point $q = q_{\mathrm{S}}^{*}$, that fluctuation effects begin to play a dominating role in the system under consideration.

The existence of the secondary phase transitions in the melt of an anti-symmetric block copolymer (which basically can be either first- or second-order) may be explained by the competition of modes corresponding to two minima of the spinodal function $H\left(q\right)$. In the region of values of parameter χ where two one-scale mesophases constructed from wave vectors with distinct moduli have close values of the free energy, the two-scale mesophase proves to be energetically beneficial as compared to any one-scale mesophase.

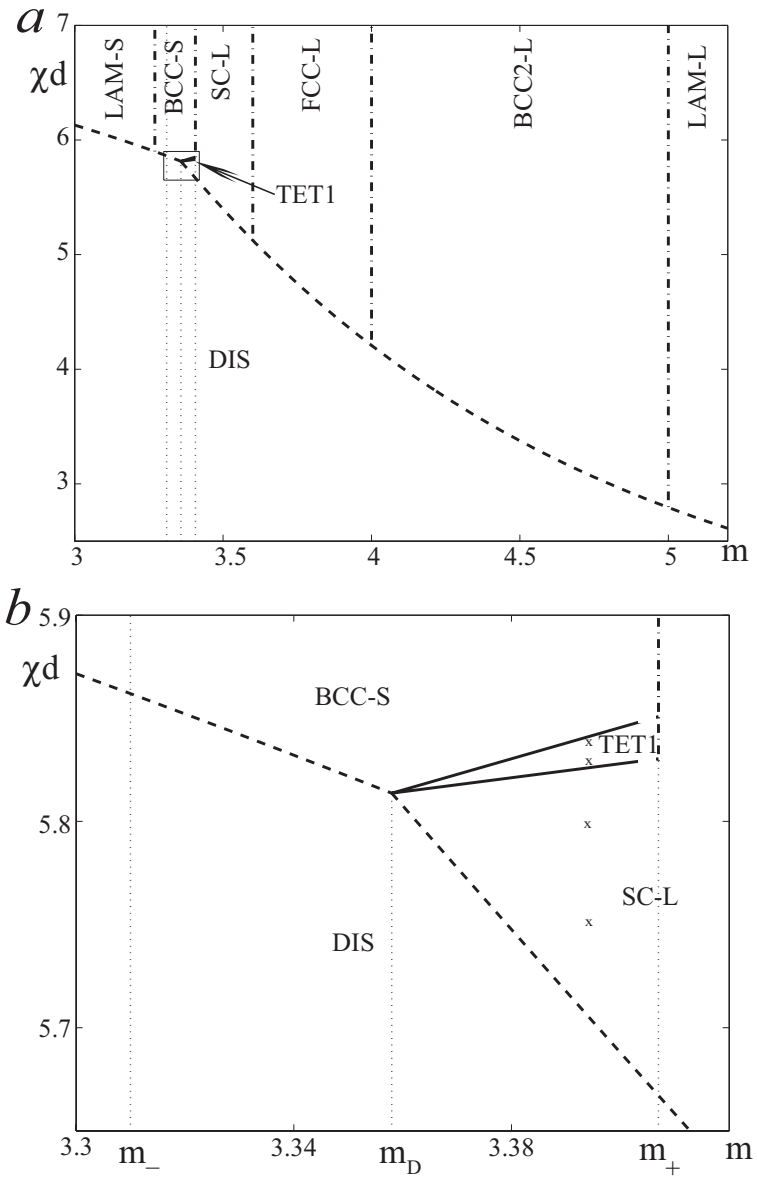

Fig. 6. Morphology diagram of the multiblock copolymer depicted in Fig.2 at $n = 6$. Full and dashed lines denote lines of first and second order phase transitions, respectively. Dash-dotted lines separate the boundaries of the regions of the mesophases' stability, while dotted lines corresponds to the inner region of the cusp (Fig.5) and double spinodal point. A part of figure *a* inside the rectangle is shown in enlarged scale in figure *b*. Here crosses denote the points at which extremal values of the OP of the stable mesophase presented in Table 1,2 have been calculated.

The spatial symmetry of the periodic function $\psi(\mathbf{r})$ of an arbitrary mesophase can be unambiguously characterized by specifying the location of its extremal points in

the three-dimensional Euclidean space. Thus the description of the symmetry of the continuous OP reduces to that of the symmetry of a discrete crystal lattice with the atoms of different sorts. Each of them is associated with a particular extremal specified by the number *S* of positive eigenvalues of the Hess matrix of the function $\psi(\mathbf{r})$ calculated at the extremal. At maxima of the function $\psi(\mathbf{r})$ describing some mesophase, this number $d = 1, 2, 3$ (known as signature) coincides with the Euclidean dimensionality of the crystal lattice of the mesophase in hand. The number *S* vanishes at its minima and assumes one of the values from 1 to ($d-1$) at the saddle points of this function. Therefore, for the three-dimensional mesophases ($d = 3$) two types of the saddles should be distinguished.

As is customary in the crystallography [34,35], to specify a k-atomic crystal lattice, one is supposed to indicate along with the type of the Bravais cell, characterizing the translation symmetry of this lattice, also its basis. The latter represents the set of m vectors pointing to the positions of all atoms located inside this cell. The number of ways in which the Bravais cell can be chosen is known to coincide with number l of the classes of equivalence (i.e., orbits of the spatial group) of different sort atoms. Essentially, the value m is the same for all the Bravais cells of any crystal lattice, though their basises, generally speaking, are different. In the general case, numbers k, l and m satisfy the following inequalities $k \le l \le m$.

For the crystal lattices of the extremal points of the function $\psi(\mathbf{r})$, the extremals of distinct signature play the role of the atoms of different sorts. That is why the lattices of the three-dimensional mesophases will be four-atomic ($k = 4$). As it follows from Figs.7,8, the Bravais cell of the lattice of the SC-L mesophase can be chosen in four manners ($l = 4$), whereas for the lattice of the TET1 mesophase, there are six options ($l = 6$) to choose the Bravais cell. The basises for the cells of both mesophases consist of eight vectors ($m = 8$). They are presented for one of the Bravais cells of the SC-L mesophase and that of the TET1 mesophase in Figs.9 and 10, respectively.

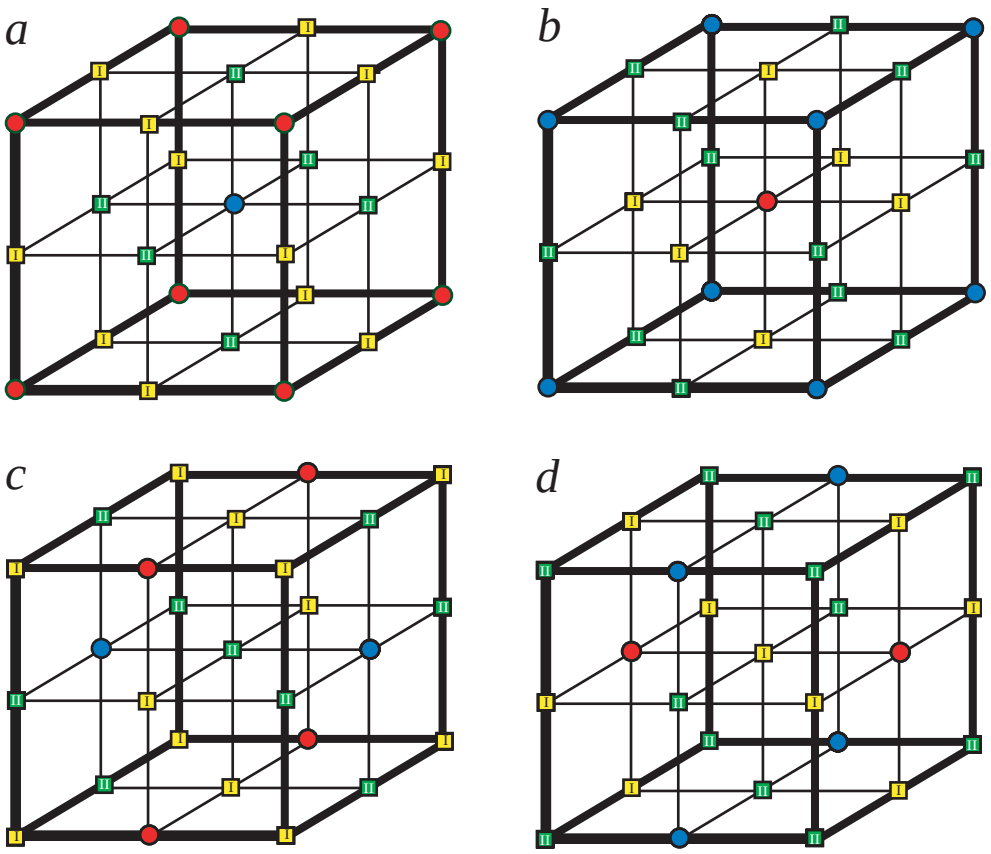

Fig. 7. The complete set of the Bravais cells of the SC-L mesophase. Position of maxima (*red circles*), minima (*blue circles*) and saddles of two signatures (*yellow and green squares*) of the order parameter function $\psi(\mathbf{r})$ for the SC-L mesophase. The Roman numerals are introduced to distinguish saddles belonging to different equivalence classes.

Calculating the values of the function $\psi(\mathbf{r})$ at its extremals at varying temperature (parameter χ), it is possible to get an information on the evolution of the metric properties of the density distribution of the monomeric units. The inspection of Table 1 shows that the distribution of OP $\psi(\mathbf{r})$ describing the one-scale SC-L mesophase, reduced to its maximum value, is independent of the parameter χ. At the same time, Table 2 demonstrates that for the two-scale TET1 mesophase, the OP values at saddle points do not remain unaltered with the increase of this parameter. Such a property, being common to any two-scale mesophase, is absent in the mesophases with only one scale of their space periodicity.

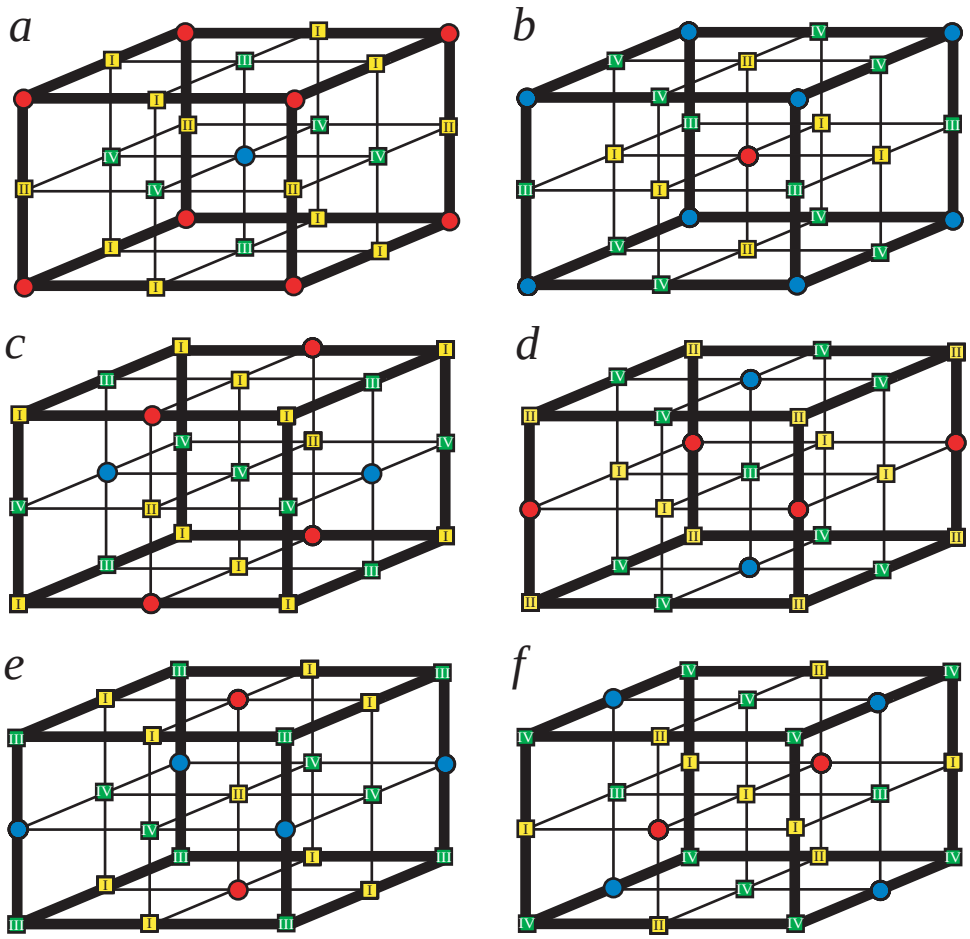

Fig. 8. Just the same as in Fig.7, but applied to TET1 mesophase.

It can be easily seen from Fig.8 that the spatial distribution of every monomeric unit M_1 and M_2 densities in the TET1 mesophase can be presented as a modulation of the OP distribution $\psi(\mathbf{r})$ corresponding to the plane SQ-L mesophase. So, the wave vector with the modulus $q = q_S^*$ of the modulating wave is perpendicular to the vectors of the translations of the crystal lattice of the SQ-L mesophase.

It is of interest to compare the results presented in this Section for periodic two-scale block copolymer (Fig.2) with those reported in paper [40] for the melt of finite two-scale block copolymers. The architecture of those macromolecules is similar to the architecture of the elementary cell depicted in Fig.2, and is also characterized by two

structural parameters m and n, whose meaning is similar to that of the parameters used in this paper. The classification diagram of the spinodal function of such a system is virtually similar to the classification diagram presented in Fig.4. When comparing the morphology diagrams of the two above-mentioned systems, it should be borne in mind that the two-component OP (23) is not considered in the framework of the approach employed in the paper [40]. That is why this approach does not claim to provide a description of the phase behavior in the region of the structure parameters falling inside the cusp. As for the morphology diagram obtained there [40] in the region of the values of structure parameters laying outside the cusp, it almost coincides qualitatively with the diagram of Fig.6. The only distinction of the morphology diagram we calculated in this region is the presence of the BCC-S mesophase.

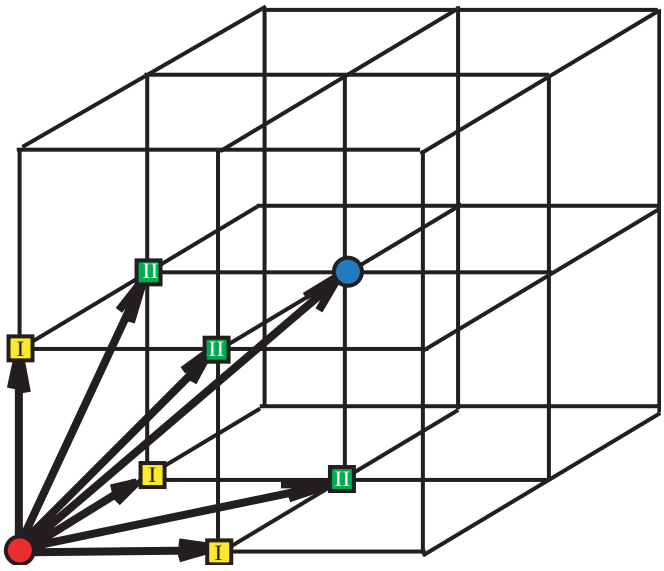

Fig. 9. The set of basis vectors for the Bravais cell depicted in Fig.7a.

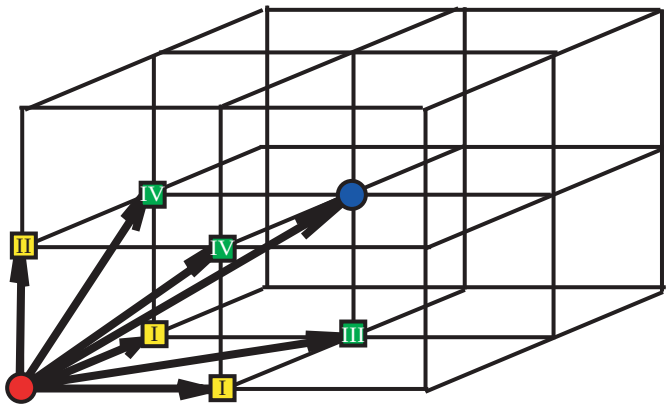

Fig. 10. The set of basis vectors for the Bravais cell depicted in Fig.8a.

Tab. 1. Value of the OP $\psi(\mathbf{r})$ (reduced to its value in the maximum) for the extremal points of the density distribution of the monomeric units in SC-L mesophase (Fig.7).

χd	Max	Saddles		Min
		I	II	
5.75	1	1/3	-1/3	-1
5.80	1	1/3	-1/3	-1

Tab. 2. Value of the OP $\psi(\mathbf{r})$ (reduced to its value in the maximum) for the extremal points of the density distribution of the monomeric units in TET1 mesophase (Fig.8).

χd	Max	Saddles				Min
		I	II	III	IV	
5.8141	1	0.236	0.382	-0.382	-0.236	-1
5.8144	1	0.103	0.448	-0.448	-0.103	-1

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Appendix A

As in the case of the tensor gfCC-2, the sum of the components of tensors $W^{(3)}_{\alpha\beta\gamma}\left(y_1,y_2\right)$ is also controlled exclusively by the length $2N$ of a macromolecule

$$\sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}\sum_{\gamma=1}^{2}W^{(3)}_{\alpha\beta\gamma}\left(y_1,y_2\right)=I^{(3)}\left(y_1,y_2\right),$$

$$I^{(3)}\left(y_1,y_2\right)\equiv 2\mathcal{N}d\,\frac{g_{\mathrm{D}}\left(2\mathcal{N}y_1\right)-g_{\mathrm{D}}\left(2\mathcal{N}y_2\right)}{y_2-y_1},\quad y_1\neq y_2 \qquad \text{(A1)}$$

$$I^{(3)}\left(y_1,y_2\right)\equiv-\left(2\mathcal{N}\right)^2 d\,g_{\mathrm{D}}{}'\left(2\mathcal{N}y_1\right),\qquad y_1=y_2$$

where δ_{ij} is Kronecker delta, while the prime denotes differentiation.

Anti-symmetric macromolecules

$$W^{(3)}_{111}\left(y_1,y_2\right)=W^{(3)}_{222}\left(y_2,y_1\right),\quad W^{(3)}_{112}\left(y_1,y_2\right)=W^{(3)}_{122}\left(y_2,y_1\right),$$
$$W^{(3)}_{211}\left(y_1,y_2\right)=W^{(3)}_{221}\left(y_2,y_1\right),\quad W^{(3)}_{121}\left(y_1,y_2\right)=W^{(3)}_{212}\left(y_2,y_1\right) \qquad \text{(A2)}$$

From relationships (20) it follows that for anti-symmetric block copolymers only four components of the tensor-function $\tilde{\theta}^{(3)}_{\alpha\beta\gamma}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)$ are independent

$$\tilde{\theta}^{(3)}_{111}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)=\tilde{\theta}^{(3)}_{222}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right),\quad \tilde{\theta}^{(3)}_{112}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)=\tilde{\theta}^{(3)}_{221}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right),$$
$$\tilde{\theta}^{(3)}_{211}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)=\tilde{\theta}^{(3)}_{122}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right),\quad \tilde{\theta}^{(3)}_{121}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)=\tilde{\theta}^{(3)}_{212}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) \qquad \text{(A3)}$$

1) $q_1 = q_2 = q_3 = q_{\mathrm{L}}$

Independent are two components of this tensor-function

$$\tilde{\theta}^{(3)}_{111}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{222}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right),$$

$$\tilde{\theta}^{(3)}_{121}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{212}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{112}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tag{A4}$$

$$\tilde{\theta}^{(3)}_{221}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{211}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{122}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)$$

2) $q_1 = q_2 = q_{\mathrm{L}}, \quad q_3 = q_{\mathrm{S}}$

Independent are three components of this tensor-function

$$\tilde{\theta}^{(3)}_{111}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{222}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right), \quad \tilde{\theta}^{(3)}_{112}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{221}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right),$$

$$\tilde{\theta}^{(3)}_{211}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{122}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{121}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{212}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) \tag{A5}$$

Symmetric macromolecules

$$W^{(3)}_{111}\left(y_1,y_2\right) = W^{(3)}_{111}\left(y_2,y_1\right), \quad W^{(3)}_{222}\left(y_1,y_2\right) = W^{(3)}_{222}\left(y_2,y_1\right),$$

$$W^{(3)}_{121}\left(y_1,y_2\right) = W^{(3)}_{121}\left(y_2,y_1\right), \quad W^{(3)}_{212}\left(y_1,y_2\right) = W^{(3)}_{212}\left(y_2,y_1\right), \tag{A6}$$

$$W^{(3)}_{112}\left(y_1,y_2\right) = W^{(3)}_{211}\left(y_2,y_1\right), \quad W^{(3)}_{122}\left(y_1,y_2\right) = W^{(3)}_{221}\left(y_2,y_1\right)$$

It is evident from these formulas that functions $W^{(3)}_{111}, W^{(3)}_{222}, W^{(3)}_{121}, W^{(3)}_{212}$ are invariant with respect to the permutation of the variables. The formula for the components of the tensor-function $\tilde{\theta}^{(3)}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)$ for symmetric block copolymers, is simplified [23]

$$\tilde{\theta}^{(3)}_{\alpha\beta\gamma}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = 2\left[W^{(3)}_{\alpha\beta\gamma}\left(y_1,y_3\right) + W^{(3)}_{\alpha\gamma\beta}\left(y_1,y_2\right) + W^{(3)}_{\beta\alpha\gamma}\left(y_2,y_3\right)\right] \tag{A7}$$

In the general case, all eight components of this tensor-function are independent

1) $q_1 = q_2 = q_3 = q_{\mathrm{L}}$

By virtue of relationships

$$\tilde{\theta}^{(3)}_{112}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{121}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{211}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right),$$

$$\tilde{\theta}^{(3)}_{122}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{212}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{221}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) \tag{A8}$$

only four components of this tensor-function are independent.

2) $q_1 = q_2 = q_{\mathrm{L}}, \quad q_3 = q_{\mathrm{S}}$

In view of relationships

$$\tilde{\theta}^{(3)}_{121}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{211}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right),$$
$$\tilde{\theta}^{(3)}_{122}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) = \tilde{\theta}^{(3)}_{212}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right) \qquad \text{(A9)}$$

only six components of this tensor-function are independent.

Appendix B

The sum of all components of the tensor $W^{(4)}_{\alpha\beta\gamma\delta}\left(y_1,y_2,y_3\right)$ is given by

$$\sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}\sum_{\gamma=1}^{2}\sum_{\delta=1}^{2} W^{(4)}_{\alpha\beta\gamma\delta}\left(y_1,y_2,y_3\right) = I^{(4)}\left(y_1,y_2,y_3\right)$$

$$I^{(4)}\left(y_1,y_2,y_3\right) \equiv 2Nd\left[\frac{g_{\mathrm{D}}\left(2Ny_1\right)}{\left(y_2-y_1\right)\left(y_3-y_1\right)} + \frac{g_{\mathrm{D}}\left(2Ny_2\right)}{\left(y_2-y_1\right)\left(y_2-y_3\right)} + \frac{g_{\mathrm{D}}\left(2Ny_3\right)}{\left(y_3-y_2\right)\left(y_3-y_1\right)}\right],$$
$$\left(y_1 \neq y_2 \neq y_3\right)$$

$$I^{(4)}\left(y_1,y_2,y_3\right) \equiv 2Nd\left[\frac{g_{\mathrm{D}}\left(2Ny_3\right)}{\left(y_3-y_1\right)^2} - \frac{2Ng_{\mathrm{D}}{}'\left(2Ny_1\right)}{\left(y_3-y_1\right)}\right], \quad \left(y_1 = y_2 \neq y_3\right) \qquad \text{(B1)}$$

$$I^{(4)}\left(y_1,y_2,y_3\right) \equiv 2Nd\left[\frac{g_{\mathrm{D}}\left(2Ny_1\right)}{\left(y_2-y_1\right)^2} - \frac{2Ng_{\mathrm{D}}{}'\left(2Ny_2\right)}{\left(y_2-y_1\right)}\right], \quad \left(y_1 \neq y_2 = y_3\right)$$

$$I^{(4)}_{\mathrm{D}}\left(y_1,y_2,y_3\right) \equiv \left(2N\right)^3 d\, g_{\mathrm{D}}{}''\left(2Ny_1\right), \quad \left(y_1 = y_2 = y_3\right)$$

Anti-symmetric macromolecules

Obviously, in this case the following conditions are satisfied

$$W^{(4)}_{1111}\left(y_1,y_2,y_3\right) = W^{(4)}_{2222}\left(y_3,y_2,y_1\right), \quad W^{(4)}_{1112}\left(y_1,y_2,y_3\right) = W^{(4)}_{1222}\left(y_3,y_2,y_1\right),$$
$$W^{(4)}_{1121}\left(y_1,y_2,y_3\right) = W^{(4)}_{2122}\left(y_3,y_2,y_1\right), \quad W^{(4)}_{1211}\left(y_1,y_2,y_3\right) = W^{(4)}_{2212}\left(y_3,y_2,y_1\right),$$
$$W^{(4)}_{2111}\left(y_1,y_2,y_3\right) = W^{(4)}_{2221}\left(y_3,y_2,y_1\right), \quad W^{(4)}_{1122}\left(y_1,y_2,y_3\right) = W^{(4)}_{1122}\left(y_3,y_2,y_1\right), \qquad \text{(B2)}$$
$$W^{(4)}_{1212}\left(y_1,y_2,y_3\right) = W^{(4)}_{1212}\left(y_3,y_2,y_1\right), \quad W^{(4)}_{2112}\left(y_1,y_2,y_3\right) = W^{(4)}_{1221}\left(y_3,y_2,y_1\right)$$

From relationships (B2) it ensues that for anti-symmetric block copolymers, only eight components of the tensor $\tilde{\theta}^{(4)}_{\alpha\beta\gamma\delta}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)$ are independent

$$\begin{aligned}
&\tilde{\theta}^{(4)}_{1111}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\tilde{\theta}^{(4)}_{2222}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right), \quad \tilde{\theta}^{(4)}_{1112}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\tilde{\theta}^{(4)}_{2221}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right),\\
&\tilde{\theta}^{(4)}_{1121}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\tilde{\theta}^{(4)}_{2212}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right), \quad \tilde{\theta}^{(4)}_{1211}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\tilde{\theta}^{(4)}_{2122}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right),\\
&\tilde{\theta}^{(4)}_{2111}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\tilde{\theta}^{(4)}_{1222}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right), \quad \tilde{\theta}^{(4)}_{1122}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\tilde{\theta}^{(4)}_{2211}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right),\\
&\tilde{\theta}^{(4)}_{1212}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\tilde{\theta}^{(4)}_{2121}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right), \quad \tilde{\theta}^{(4)}_{2112}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)=\tilde{\theta}^{(4)}_{1221}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)
\end{aligned} \tag{B3}$$

Symmetric macromolecules

$$\begin{aligned}
&W^{(4)}_{1111}\left(y_1,y_2,y_3\right)=W^{(4)}_{1111}\left(y_3,y_2,y_1\right), \quad W^{(4)}_{2222}\left(y_1,y_2,y_3\right)=W^{(4)}_{2222}\left(y_3,y_2,y_1\right),\\
&W^{(4)}_{1112}\left(y_1,y_2,y_3\right)=W^{(4)}_{2111}\left(y_3,y_2,y_1\right), \quad W^{(4)}_{1121}\left(y_1,y_2,y_3\right)=W^{(4)}_{1211}\left(y_3,y_2,y_1\right),\\
&W^{(4)}_{1122}\left(y_1,y_2,y_3\right)=W^{(4)}_{2211}\left(y_3,y_2,y_1\right), \quad W^{(4)}_{2221}\left(y_1,y_2,y_3\right)=W^{(4)}_{1222}\left(y_3,y_2,y_1\right),\\
&W^{(4)}_{2212}\left(y_1,y_2,y_3\right)=W^{(4)}_{2122}\left(y_3,y_2,y_1\right), \quad W^{(4)}_{1212}\left(y_1,y_2,y_3\right)=W^{(4)}_{2121}\left(y_3,y_2,y_1\right),
\end{aligned} \tag{B4}$$

It is apparent from formulas (B4) that the functions $W^{(4)}_{1111}$ and $W^{(4)}_{2222}$ are symmetric with respect to inversion $y_1 \leftrightarrow y_3$. The formula for the components of the tensor-function $\tilde{\theta}^{(4)}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4\right)$ for symmetric block copolymers reduces to

$$\begin{aligned}
\tilde{\theta}^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}\left(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3\right)=2\Big[&W^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}\left(y_1,p_1,y_4\right)+W^{(4)}_{\alpha_1\alpha_2\alpha_4\alpha_3}\left(y_1,p_1,y_3\right)+\\
&W^{(4)}_{\alpha_2\alpha_1\alpha_4\alpha_3}\left(y_2,p_1,y_3\right)+W^{(4)}_{\alpha_2\alpha_1\alpha_3\alpha_4}\left(y_2,p_1,y_4\right)+\\
&W^{(4)}_{\alpha_1\alpha_3\alpha_4\alpha_2}\left(y_1,p_2,y_2\right)+W^{(4)}_{\alpha_1\alpha_3\alpha_2\alpha_4}\left(y_1,p_2,y_4\right)+\\
&W^{(4)}_{\alpha_2\alpha_4\alpha_1\alpha_3}\left(y_2,p_2,y_3\right)+W^{(4)}_{\alpha_3\alpha_1\alpha_2\alpha_4}\left(y_3,p_2,y_4\right)+\\
&W^{(4)}_{\alpha_1\alpha_4\alpha_3\alpha_2}\left(y_1,p_3,y_2\right)+W^{(4)}_{\alpha_1\alpha_4\alpha_2\alpha_3}\left(y_1,p_3,y_3\right)+\\
&W^{(4)}_{\alpha_2\alpha_3\alpha_1\alpha_4}\left(y_2,p_3,y_4\right)+W^{(4)}_{\alpha_3\alpha_2\alpha_1\alpha_4}\left(y_3,p_3,y_4\right)\Big]
\end{aligned} \tag{B5}$$

Appendix C

By virtue of the independence of only one component $W_{\alpha\beta}^{(2)}(y)$ of the tensor $W^{(2)}(y)$, it is enough to present the expression for the function $R_{11}^{(2)}(y)$ (13) only

$$
\begin{aligned}
&R_{11}^{(2)}(y)=\frac{1}{2L}\sum_{i=1}^{5}r_i(y)\\
&r_1(y)=ng_{\mathrm{D}}(y),\quad r_2(y)=ne^{-y}\varphi^2(y)z_n(y)\\
&r_3(y)=2nme^{-y}h(my)h(2ny)\varphi(y)\\
&r_4(y)=\frac{m^2}{2}g_{\mathrm{D}}(my),\quad r_5(y)=n^2e^{-(m+2)y}h^2(2ny)\varphi^2(y)\\
&h(y)\equiv\frac{1-e^{-y}}{y},\quad \varphi(y)\equiv\frac{2}{1+e^{-y}},\quad z_n(y)\equiv\frac{h(2y)-h(2ny)}{y}
\end{aligned}
\qquad \text{(C1)}
$$